

THE PROBLEM OF THE VOLATILITY OF NIOBIUM OXIDES

I.V.Golubtsov, A.V.Lapitskiy, and V.K.Shiryayev

FACILITY FORM 608	N66 33681	
	(ACCESSION NUMBER)	(THRU)
	12 (PAGES)	06 (CODE)
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Translation of "K voprosu o letuchesti okislov niobiya".
Izvestiya Vysshikh Uchebnykh Zavedeniy SSSR, Khimiya i
Khimicheskaya Tekhnologiya, No.4, pp.571-574, 1960.

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 1.00Microfiche (MF) .50

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON JUNE 1966

THE PROBLEM OF THE VOLATILITY OF NIOBIUM OXIDES

**/571

I.V.Golubtsov, A.V.Lapitskiy, and V.K.Shiryayev*

3 3681

Investigations on the volatility of niobium oxide, by measuring the saturated vapor pressure of niobium dioxide and pentoxide, in a Knudsen effusion chamber, at 1489 to 1905°K with radioactive Nb⁹⁵ as tracer, are discussed. Block diagrams of the modified HF-heated vacuum unit with quartz collector, and tabulated data of the measured vapor pressures of niobium oxides are given. Niobium pentoxide in air at 1350°C does not evaporate, while it undergoes thermal dissociation in vacuum above 1150°C in accordance with the equation: $\text{Nb}_2\text{O}_5 = 2 \text{NbO}_2 + \frac{1}{2} \text{O}_2$.

The current literature contains only fragmentary information on the volatility of niobium oxides. For example, Kolchin et al. (Bibl.1) assert that the lower oxides of niobium have a noticeable volatility at 1700°C and a relatively high volatility at 1850°C. Unfortunately, their report gives no data on the composition of the oxides and on the characteristics of the vapor pressure of the oxides mentioned.

In the present work, an attempt was made to measure the saturated vapor pressure of niobium pentoxide and niobium dioxide in the temperature range of 1489 - 1905°K with the use of radioactive Nb⁹⁵.

*M.V.Lomonosov State University, Moscow, Radiochemistry Laboratory. Paper presented at the First Interinstitute of Higher Learning Conference on Radiochemistry, April 20-25, 1959, Moscow.

** Numbers in the margin indicate pagination in the original foreign text.

Experimental Part

On the basis of literature data (Bibl.2, 3) and the observations by the authors, one can say that niobium oxides belong to the class of comparatively difficultly volatilizable compounds. For this reason and to increase the accuracy of the measurements as well as the sensitivity of the method, we used Nb^{95} .

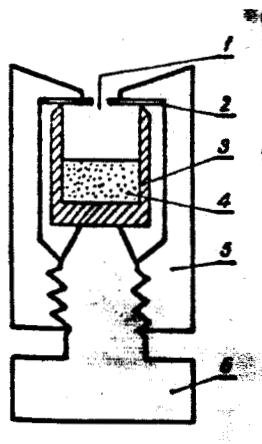


Fig.1 Effusion Chamber

- 1 - Effusion orifice; 2 - Diaphragm; 3 - Vessel with specimen; 4 - Investigated substance; 5 - Chamber casing; 6 - Spring-filled plug.

To perform the experiment we constructed a device with high-frequency heating, using a vacuum unit and an MVP-3M generator with an auxiliary oscillatory loop. The vacuum unit produced a vacuum of the order of 1×10^{-5} to 5×10^{-6} mm Hg in the system, when the specimens were heated to $1500 - 1600^\circ$.

The sample to be tested was placed in a Knudsen effusion chamber (Bibl.4) constructed especially for this experiment (Fig.1). The working portions of the chamber (vessel and diaphragm) were interchangeably made of molybdenum, tungsten, and high-temperature ceramics. For evaporation, a quartz and tungsten device was selected (Fig.2). The vapor collector was connected with the vacuum unit over a ground joint and provided with a circulating water jacket for cool-

ing the inside surface of the collector. A window of fused polished quartz was sealed into the upper part of the cylinder. Into the quartz collector, slightly below the window, a quartz screen was inserted through the ground joint, /572 to prevent deposition of oxides on the window. At the start of the experiment, we exhausted the device to a pressure of 10^{-5} mm Hg and then heated the chamber to the prescribed temperature by a high-frequency current. Usually this operation took 20 - 30 sec. For starting the exposure, we used the instant at which

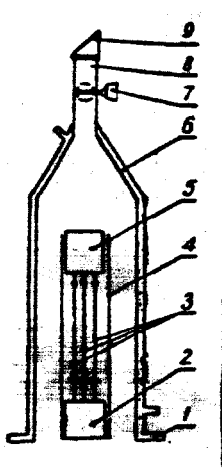


Fig.2 Quartz Instrument

- 1 - Plane ground joint; 2 - Baseplate of unit;
- 3 - Tungsten holders; 4 - Radiation shield;
- 5 - Effusion chamber; 6 - Water jacket;
- 7 - Ground joint with protective screen;
- 8 - Quartz tube; 9 - Optical exit with prism.

the prescribed temperature was reached and for stopping the experiment, the cutoff of the HF generator. In the experiments with niobium dioxide the air was not allowed to enter the device immediately after the final cooling but some time later so as to avoid oxidation to niobium pentoxide. The temperature of the effusion chamber was measured by an OPIIR-09 optical pyrometer.

To measure the saturated vapor pressure of niobium pentoxide, we used the flow method in addition to the Knudsen method. These experiments were carried

out with a setup consisting of an MVP-3M furnace, a reaction tube, an air drying unit, and a Patrikeyev UGSP-1 gasometer system. A corundum crucible with a weighed sample of niobium pentoxide was placed in the reaction tube.

To obtain the initial preparations labeled with Nb^{95} , we used metallic niobium powder containing trace impurities of iron, titanium, silicon, tin, and tantalum. The niobium was converted to oxide and then to an oxalate complex; after adding Nb^{95} to the solution, it was precipitated with tannin and roasted to the pentoxide. Niobium dioxide was obtained from the active pentoxide and metallic niobium, used at a ratio of 2:1, in a TGV-1 furnace at a vacuum of 10^{-4} mm Hg with heating of this mixture in an alundum crucible for 10 hrs at about 1250°C . Using the same method, we simultaneously obtained an inert dioxide which was identified from its X-ray pattern. The Debye powder diagram confirmed the formation of niobium dioxide, with very small residual quantities of the initial high-temperature modification of niobium pentoxide.

The specific activity of the obtained oxide was determined by measuring the activity on the gamma-tube of the B-2 unit. The substance that had precipitated on the collector was washed off with small amounts of hot concentrated sulfuric acid. Washing was performed three times. The last portion of the acid showed no activity. The sulfuric acid was carefully evaporated in a dish for counting.

The vapor pressure was calculated by the formula

$$P = 17.14 \frac{m}{StK} \sqrt{\frac{t}{M}} \quad \text{for} \quad \frac{m}{m_0} = \frac{I}{I_0},$$

where m denotes the mass of the volatile fraction with an activity I ; m_0 is the weight of a standard with an activity I_0 ; K is the Clausing coefficient; t is the exposure time; M is the molecular weight; S is the area of the effusion orifice, in cm^2 .

The data obtained are shown in Table 1 and in Fig.3.

To determine the stability of niobium dioxide in vacuum in contact with molybdenum, we recorded the X-ray pattern of a specimen heated at 1300° for 1573 2 hrs. Identification of the lines showed good agreement with the literature data (Bibl.5) for niobium dioxide, which proves the constancy of this phase under experimental conditions.

TABLE 1

VAPOR PRESSURE OF NIOBIUM DIOXIDE (AREA OF EFFUSION ORIFICE $7.06 \times 10^{-2} \text{ cm}^2$, CLAUSING COEFFICIENT 0.858)

Temperature, °K	Mass of evaporated Substance, gm	Exposure time, sec	Pressure, mm Hg
1489	$1.91 \cdot 10^{-3}$	15600	$1.2 \cdot 10^{-4}$
1556	$1.12 \cdot 10^{-3}$	7200	$1.5 \cdot 10^{-4}$
1556	$1.50 \cdot 10^{-3}$	10800	$1.4 \cdot 10^{-4}$
1612	$3.20 \cdot 10^{-3}$	9000	$3.6 \cdot 10^{-4}$
1612	$3.01 \cdot 10^{-3}$	9000	$3.4 \cdot 10^{-4}$
1712	$3.89 \cdot 10^{-3}$	9000	$4.5 \cdot 10^{-4}$
1783	$7.02 \cdot 10^{-3}$	9000	$6.4 \cdot 10^{-4}$
1783	$6.78 \cdot 10^{-3}$	9000	$6.1 \cdot 10^{-4}$
1905	$1.01 \cdot 10^{-4}$	9000	$1.4 \cdot 10^{-3}$

Under the same conditions we carried out an experiment with active niobium pentoxide. The values obtained are shown in Table 2 and Fig.3.

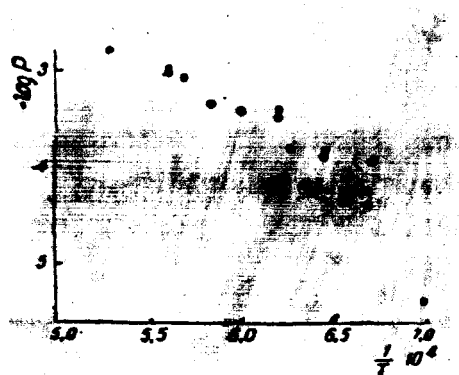


Fig.3 Vapor Pressure of Niobium Dioxide (○) and Niobium Dioxide from a Mixture of $\text{NbO}_2 + \text{Nb}_2\text{O}_5$ (●)

The coating deposited on the collector was black in color. The nature of the coating on the collector and an analysis of the experimental data of Fig.3 raises doubt as to the evaporated compound actually being Nb_2O_5 . Experiments by the flow method in an air stream showed that niobium pentoxide is nonvolatile even at 1350°C since not even traces of a radioactive coating could be detected on the collector at the high specific activity ($15 \mu/\text{gm}$) of the initial preparation. Here, the temperature was measured by a standard thermocouple.

TABLE 2

VAPOR PRESSURE OF NIOBIUM DIOXIDE OBTAINED BY THERMAL DISSOCIATION OF NIOBIUM PENTOXIDE IN VACUUM (AREA OF EFFUSION ORIFICE $1.25 \times 10^{-4} \text{ cm}^2$, CLAUSING COEFFICIENT 0.516)

Temperature, $^\circ\text{K}$	Mass of evaporated Substance, gm	Exposure time, sec	Pressure, μHg
1432	$2.01 \cdot 10^{-4}$	38400	$4.2 \cdot 10^{-4}$
1498	$2.50 \cdot 10^{-4}$	36000	$5.7 \cdot 10^{-4}$
1498	$1.25 \cdot 10^{-4}$	25560	$4.0 \cdot 10^{-4}$
1576	$1.63 \cdot 10^{-4}$	21600	$6.2 \cdot 10^{-4}$
1598	$6.83 \cdot 10^{-4}$	28800	$2.0 \cdot 10^{-4}$
1666	$7.13 \cdot 10^{-4}$	16320	$3.8 \cdot 10^{-4}$
1756	$8.16 \cdot 10^{-4}$	9000	$8.1 \cdot 10^{-4}$

Proceeding from the assumption of a possible interaction of niobium pentoxide with the chamber material, we made an X-ray phase analysis of the niobium preparations roasted both in ceramic and in tungsten boats. In both cases, the powder patterns were identical, indicating that the chamber material did not affect the stability of niobium. We also recorded the X-ray pattern of the surface layer of niobium pentoxide, taken - after heating in vacuum - from the center portion of the vessel of the effusion chamber. The X-ray pattern showed an appreciable content of niobium dioxide in the preparation.

Thus, we can consider that in vacuum at high temperatures thermal dissocia-

tion takes place, described by the equation: $\text{Nb}_2\text{O}_5 = 2\text{NbO}_2 + \frac{1}{2}\text{O}_2$; the obtained data (Table 2) actually represent the vapor pressure of niobium dioxide, but apparently for different degrees of vapor saturation in the chamber.

The authors wish to thank Yu.P.Simanov for assistance and valuable advice in the interpretation of the data of the X-ray phase analysis, and L.P.Belykh, V.A.Galushkin, and V.G.Pakhomov for aid in setting up the device.

Conclusions

1. The vapor pressure of niobium dioxide was measured in the temperature range of 1489 - 1905°K by the tracer method.

2. It was demonstrated by means of Nb^{95} that niobium pentoxide in an air stream at 1350°C does not evaporate and under these conditions is a thermally stable compound.

3. It was established that niobium pentoxide in vacuum at a temperature above 1150°C undergoes thermal dissociation in accordance with the equation:

$$\text{Nb}_2\text{O}_5 = 2\text{NbO}_2 + \frac{1}{2}\text{O}_2.$$

BIBLIOGRAPHY

1. Kolchin, P.P., Sumarokova, V.N., and Chuveleva, N.P.: At. Energ., Vol.3, p.575, 1957.
2. Süe. P.: Bull. Soc. Chim. France, Vol.6, p.823, 1939.
3. Brauer, G.: Naturwissenschaften, Vol.28, p.30, 1940.
4. Knudsen, M.: Ann. Physik, Vol.23, p.75, 1909.
5. Brauer, G.: Z. Anorg. Allgem. Chem., Vol.248, p.1, 1941.

Translated for the National Aeronautics and Space Administration by the O.W.Leibiger Research Laboratories, Inc.